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Energetic valorisation of olive mill wastewater impregnated on low cost absorbent: Sawdust versus olive solid waste

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ABSTRACT

The oil extraction industry generates two by-products, an aqueous effluent, olive mill wastewater (OMWW) and a solid residue, olive mill solid waste (OMSW). OMWW is considered as the major pollutant in the Mediterranean area causing severe environmental threats. The main problem regarding the disposal of OMWW is to find an environmental and economical viable solution. A new valorisation strategy has been carried out which includes the following steps: (a) absorption of OMWW on low-cost renewable absorbents, (b) natural evaporation of the water and (c) energy recovery by combustion of the impregnated absorbents. Sawdust and OMSW were selected as low-cost renewable absorbents. Thermal behaviour of the impregnated samples was studied under inert and oxidative atmosphere from 20 °C to 900 °C using thermogravimetric analysis (TGA). Kinetic parameters were obtained and compared for the different samples. Gaseous emissions such as CO_2, CO and volatile organic compounds (VOC) were measured under oxidative conditions at 500 °C, 600 °C and at 700 °C in a fixed bed reactor. The results indicate that for samples containing the same amount of OMWW, the reaction time of impregnated sawdust is lower compared to impregnated OMSW. Combined treatment of OMMW proposed in this study may be a promising method for the reduction of their environmental impact and for the energetic valorisation of the organic content of OMWW.

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1. Introduction

The European Union (EU) is the main producer and consumer of olive oil in the world. EU total production is 1.75 million tons, the worldwide production being around 2.3 million tons [1]. Olive oil is produced in olive mills either by the discontinuous press method or by the continuous centrifugation method.

In the last decades, development of continuous centrifugation method has been observed. This method has many advantages compared to the discontinuous press method such as complete automation and better oil quality. However, it also presents some inconveniences such as higher wastewater production, *i.e.* olive mill wastewater (OMWW). In the Mediterranean region, OMWW produced at a rate above 10 million m^3/year [2,3]. Furthermore, with chemical oxygen demand (COD) values in the range 40–220 g L^{-1} and biochemical oxygen demand (BOD) values in the range 23–100 g L^{-1}, which is 25–80 times higher than the pollution level of common municipal wastewater [4], OMWW represents a major environmental problem. Thus, the olive oil producer countries will face a serious challenge to find an environmentally and economically viable solution in handling and disposal of OMWW.

To avoid these environmental impacts, olive mills were forced to treat or eliminate this waste. Hence, a wide range of systems has been studied for the disposal or use of OMWW, such as aerobic [5] and anaerobic [6] treatments composting and direct watering on fields [7]. However, these methods present several drawbacks that make their implementation very difficult and very expensive [1,2,8].

Use of OMWW for the production of renewable energy is a potential solution due to high energy content (high heating values of 18 MJ/kg, dry basis see experimental section). Thermal processes are the main option for the treatment of large amounts of OMWW. However, due to the high water content of OMWW, its thermal

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treatment is not economically viable although combustion of concentrated OMWW with olive mill solid waste has been already studied [9–11].

Different operational procedures were therefore evaluated to recover the chemical potential of OMWW through the adsorption or the absorption on natural biopolymers or activated carbon. Activated carbon is the most widely used adsorbent because of its high adsorption capacity, but its use is limited because of its high cost [12]. This limitation has led to search for cheaper substitutes. Several biomass and biomass wastes have been investigated for the absorption of organic content of OMWW. Recently, Le Buzit et al. [13] have filed a patent concerning a new process for the treatment of aqueous effluent containing a high amount of organic matter. The main originality of this process is the simple handling and the low-cost treatment which prevents soil and groundwater pollution. This process may be applied for the treatment of OMWW (Fig. 1). It consists of the following steps: (a) absorption of the OMWW on ligneous material, (b) evaporation of the water and (c) energy recovery of the organic matter present in OMWW. Such process could be compared to the thermal pre-treatment process of biomass [14].

The aim of the present work is to compare the potential of two low cost absorbents, namely sawdust [15] and olive mill solid waste (OMSW) for the disposal of OMWW. Hence, the absorption of OMWW on low cost absorbent and the thermal behaviour of the blends obtained, impregnated sawdust (IS) and impregnated solid waste (ISW) are presented. The kinetic parameters, obtained under inert and oxidative atmosphere, are compared. Gaseous emissions of the absorbent and the blends are also compared during the isothermal combustion in a fixed bed reactor at different temperatures (500 °C, 600 °C and 700 °C). On account of these characteristics, the potential of the blends as alternative fuel fossil fuels such as coal will be evaluated.

2. Experimental procedure

2.1. Raw material

Samples of OMWW were collected from an olive oil mill (three-phase centrifugal olive mills) located at Saint Saturnin les Apt, Vaucluse, France. OMWW was maintained at 4 °C to prevent biodegradation. Pine sawdust was supplied by SPPS-France. The sawdust was sieved through 25 to 35 US Mesh size. OMSW samples used in this study were provided by a traditional batch mill from the region of Mahdia (Tunisia). The water content of OMSW was close to 10%. It was ground and sieved to ensure homogeneity. The particle size range 1–1.6 mm was selected for tests.

2.2. Sample preparation

Fig. 1 illustrates the different steps of impregnated absorbent formation. 50 g of OMWW were slowly added to 10 g of sieved absorbent in a pan and manually mixed. The layer of absorbent has a thickness less than 1 cm. The pan was then left at room temperature and periodically weighed until a constant mass was obtained to get impregnated sawdust (IS) and impregnated solid waste (ISW). The water content of both blends was close to 10% and the amount of organic matter originated from OMWW was 40 wt% for both samples.

The OMWW sample was dried in an oven at 105 ± 2 °C resulting in a sample named OMWW-DM.

2.3. Sample characterisation

The characterisation of OMWW (pH, chemical oxygen demand (COD), biological oxygen demand (BOD_5), total nitrogen, total phosphorus and total dissolved solids) was carried out by CTC Environment (Lyon, France) is shown in Table 1.

Proximate analysis measurements were conducted using a thermogravimetric analyser (CAHN 121 thermobalance) and the results are shown in Table 2. The proximate TG method involves heating the sample (under N_2) at a rate of 10 °C/min to 110 °C and then maintaining this temperature for 10 min to obtain the weight loss associated with moisture. The temperature is then ramped from 110 °C at a rate of 20 °C/min to 900 °C (under N_2) and held for 10 min to obtain the weight loss associated with volatiles release. Air is then introduced into the furnace chamber to oxidize the carbon in the char and the weight loss associated with this is the fixed carbon. The remaining material after combustion is the ash. Ultimate analyses were determined by Service Central d'Analyses (Vernaison, France) and are shown in Table 3.

Table 1
Physical, chemical and biological parameters of OMWW.

Parameters	Unit	Values
pH	–	5.3
TDS[a]	g L^{-1}	12.51
COD[b]	g L^{-1}	228
DBO_5[c]	g L^{-1}	84.2
Total nitrogen	g L^{-1}	0.51
Total phosphorus	g L^{-1}	0.94

[a] Total dissolved solids.
[b] Chemical oxygen demand.
[c] Biological oxygen demand.

Table 2
Proximate analysis of different samples.

	Proximate analysis (wt%)			
	Fixed Carbon	Volatile matter	Moisture	Ash
OMWW-DM[a]	23	63.1	1.3	12.6
Sawdust[b]	16.3	76	6.7	1.0
OMSW[b]	23.4	67.6	7	2
IS[b]	27.6	60.2	6.6	5.6
ISW[b]	23.2	59.6	11	6.2

[a] Dry basis.
[b] As-received basis.

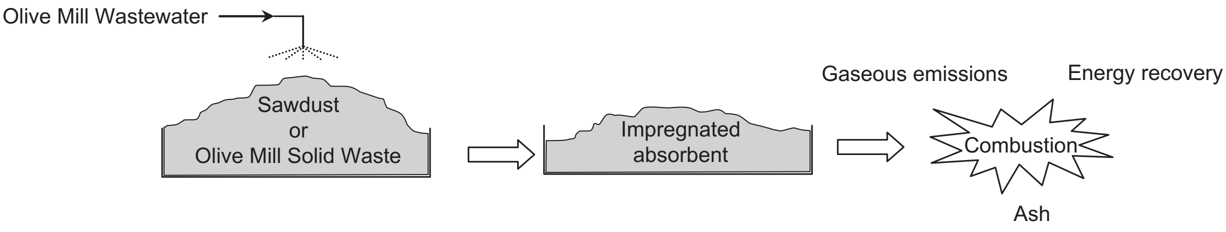

Fig. 1. Different steps of the energetic valorisation of olive mill wastewater.

Table 3
Energy contents and ultimate analysis of different samples.

	HHV ($kJ\ kg^{-1}$)[a]	Ultimate analysis (wt%)[a]		
		C	H	N
OMWW-DM	18 300	42.24	nd[b]	1.44
Sawdust	19 300	46.54	5.96	<0.30
OMSW	19.500	52.1	6.70	1.40
IS	17 900	45.30	5.73	0.44
ISW	19.000	44.80	6.07	<0.3

[a] As-received basis.
[b] Not determined.

Table 4
Concentration of the elements in g/100 g.

Sample	K	Ca	Na
OMWW-DM[a]	8.0	0.5	0.11
IS[b]	3.6	0.4	0.03
ISW[b]	3.8	0.4	0.01
Sawdust[b]	0.15	0.3	0.02
OMSW[b]	0.6	1.1	0.08

[a] Dry basis.
[b] As-received basis.

The heat produced by combustion of samples at constant volume was measured with a Prolabo type calorimeter for all samples. The Higher Heating Value (HHV) were calculated and given in Table 3. For each analysis, the reproducibility was checked by at least one duplicate run.

Elemental composition of K, Ca and Na were also analysed by flame atomic absorption spectroscopy (FAAS) using a Varian Absorption Spectrometer after microwave digestion with HNO_3.The results are shown in Table 4.

2.4. Thermogravimetic analysis

Thermogravimetric analyses (TGA) were carried out using a CAHN 121 thermobalance. Initial sample masses of 10 mg were placed in a hemispherical crucible of 4 mm of deep and 9 mm of diameter at its mouth. The use of small masses was necessary to reduce the effects of side reactions as well as mass and heat transfer limitations. Experiments were performed under nitrogen and airflow of 13 NL h^{-1} at heating rate of 5 °C min^{-1}.

2.5. Combustion tests

The combustion of the tested samples was performed in a fixed bed reactor in order to analyse their gas emissions. The experimental set-up used for the combustion of the different samples under fixed bed conditions is described in Fig. 2.

In each experiment, the fused silica frit was loaded with 100 mg of tested sample while positioned in the bottom part outside the ceramic furnace. Then a gas flow of nitrogen was injected at 50 NL h^{-1} and the heating system was connected to reach the selected set-point temperature using an automatic PID temperature controller. During this period, the temperature of bed measured by a thermocouple located 1 mm above the sample was maintained at ambient temperature using a cooling system. Once the set-point temperature had been reached, a gas flow of air (20% of O_2 and 80% of N_2) was injected at 50 NL h^{-1} and the reactor was introduced rapidly into the heating zone of the tubular furnace. The heating of samples can be considered instantaneous, since gas emissions evolved as soon as the reactor was inserted in the tubular furnace.

Mole fractions of CO_2, CO at the reactor outflow were measured by infrared analysers (Rosemount Binos 100 or NGA 2000). The total emission of VOC was analysed using a flame ionisation

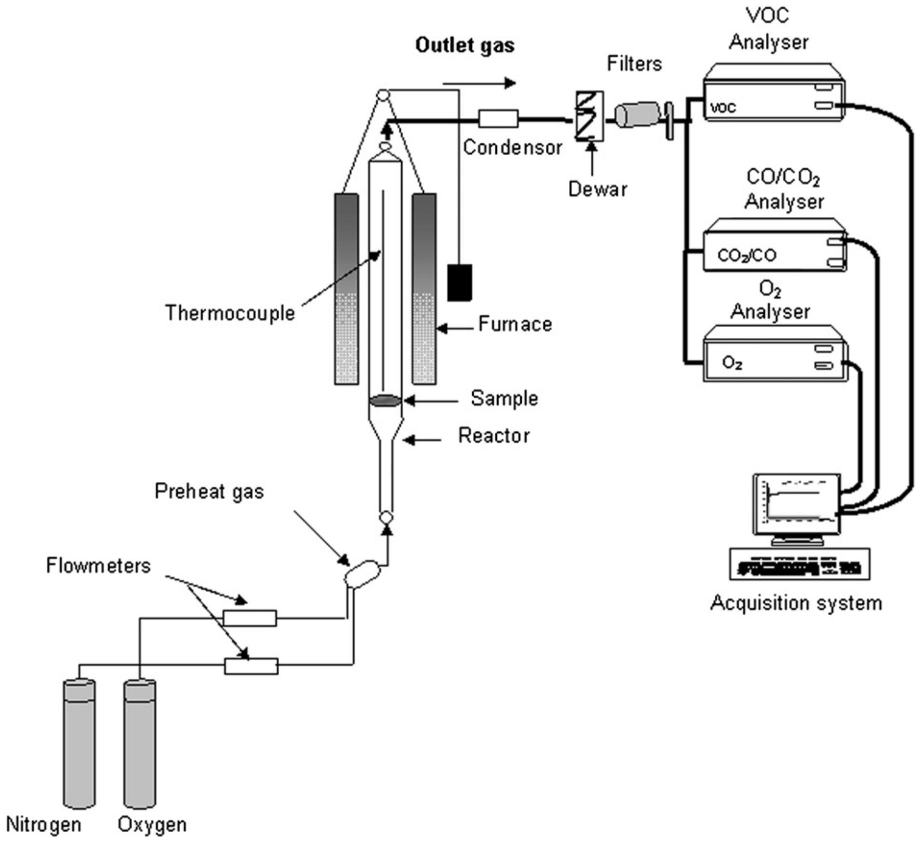

Fig. 2. Experimental set-up.

detector (FID) placed online in the exhaust. FID analyser was standardized with methane and VOC concentration is expressed in methane equivalent in the outlet. Gas composition was recorded every 2 s.

3. Results and discussion

Two types of low-cost renewable absorbents have been evaluated: sawdust and OMSW. The high surface area of sawdust allows an efficient evaporation of the water content under normal atmospheric conditions and also removes odours associated with the OMWW [13,16]. Furthermore, oil residues are preferentially absorbed on absorbents and thus do not limit the evaporation of water.

3.1. *Pyrolytic behaviour*

Pyrolysis profiles under inert atmosphere (Residual weight TG and derivative weight loss DTG) of the different samples are reported in Fig. 3. It is seen that TG and DTG profiles of sawdust, OMSW and OMWW-DM are similar to those described in literature [10,17,18].

TG and DTG curves of IS are quite similar to those of OMWW-DM and they reveal that the IS sample follows the same pyrolysis process as OMWW-DM. In fact, the devolatilization of the IS sample starts at the same temperature as OMWW-DM (125 °C). Therefore, the absorption of the OMWW organic content on sawdust allows the thermal decomposition of cellulosic compounds at lower temperatures. This result can be explained by the characteristics of the organic compounds present in OMWW. Several authors confirmed that the degradation of lignin containing polyphenol structures starts at a lower temperature [17,18].

The devolatilization step finishes earlier (296 °C) for OMWW-DM compared to IS (350 °C). This behaviour may be related to the original composition of IS being richer in cellulose (41.5%). Likewise, the temperature corresponding to the maximum mass loss of OMWW-DM (235 °C) is lower for IS (273 °C). However, IS and OMWW-DM have a similar measured maximum mass loss rate (0.055% s^{-1}).

Behaviour of ISW is similar to that of OMSW. As in both cases, their devolatilization occurred between 150 °C and 340 °C. This step characterizes the removal of the volatile matter and the formation of char. In this range, two decomposition processes are distinguished, with two maximum weight loss rates appearing at 244 °C and at 312 °C. These correspond to the degradation of hemicellulose and cellulose, respectively. The presence of two peaks for ISW is attributed to the initial composition of olive mill solid waste. Since OMSW has an equal amount of hemicellulose and cellulose, ISW has two maximum weight mass loss rates related to the presence of these two components in the impregnated sample.

The char formation step of impregnated samples (IS and ISW) takes place over a closer temperature range compared to the other steps. The end temperature of this step is 500 °C for IS and ISW.

Residual masses at 850 °C are 33% (±1) of the initial mass for OMWW-DM, (30% ± 2) for IS, (28.5% ± 0.2) for ISW, (24% ± 1) for OMSW and (16.5% ± 0.3) for sawdust. With regard to relative standard deviation, OMWW-DM and IS present high residual mass at 850 °C. Compared to sawdust, the presence of OMWW in the samples increases the residual mass yield at the end of the pyrolysis (850 °C). This behaviour may be due to the presence of

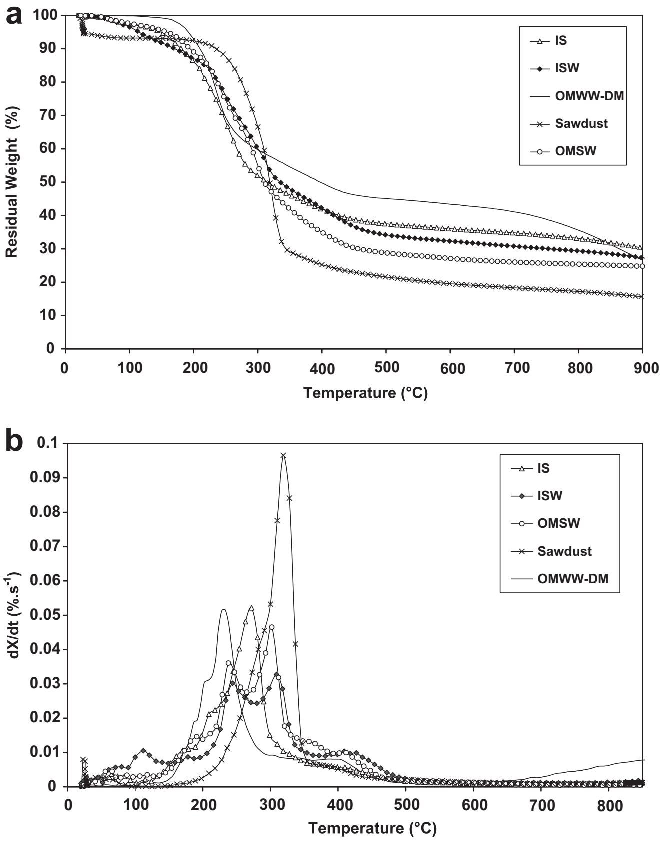

Fig. 3. TG (a) and DTG (b) curves of different samples under inert atmosphere at 5 °C min^{-1}.

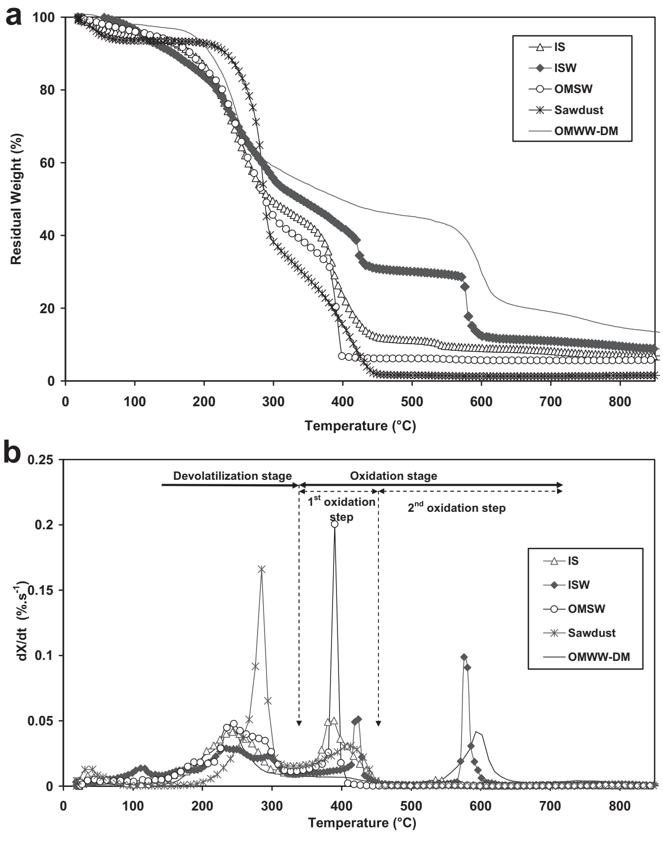

Fig. 4. TG (a) and DTG (b) curves of different samples under oxidative atmosphere at 5 °C min^{-1}.

Table 5
IS and ISW behaviour during char oxidation stage.

Sample	Char oxidation stage								
	1st step of oxidation				2nd step of oxidation				
	Temperature range (°C)	Mass loss (%)	T_1 at V_{1max} (°C)	V_{1max} (% s^{-1})	Temperature range (°C)	Mass loss (%)	T_2 at V_{2max} (°C)	V_{2max} (% s^{-1})	Ash at 850 °C (%)
IS	300–460	37.7	385	0.055	460–570	2.4	541	0.0064	6(±1)
ISW	332–500	20.7	423	0.055	500–620	18.6	522	0.1180	8.5(±0.6)

polyaromatic compounds which need higher temperature to be thermally destroyed [17,18].

Furthermore, with regard to literature [2,19] and our study (Table 4), OMWW has a high inorganic salt content which may explain the high amount of ash in the impregnated sample.

3.2. Oxidative behaviour

The TG and DTG curves of IS, ISW, sawdust, OMWW-DM and OMSW under oxidative atmosphere are presented in Fig. 4. The sawdust oxidation follows a classic biomass profile [20–24]. The temperature range of sawdust devolatilization is 180–340 °C, while its oxidation finishes at about 460 °C.

OMSW oxidation follows a classic olive solid residue profile as found in the literature [25,26]. Thermal degradation under oxidative atmosphere of OMWW-DM also occurs in two main steps, as for sawdust, with different temperature ranges. In fact, devolatilization of OMWW-DM proceeds between 125 °C and 450 °C, followed by a char oxidation between 450 °C and 650 °C. The DTG profile of OMWW is similar to those of previous studies [11].

When the organic content of OMWW was absorbed on biomass, thermal oxidation of impregnated samples proceeded differently. Devolatilization still occurs within the same temperature range for the IS and ISW. This stage is followed by two oxidation steps in the temperature range of 300 °C–620 °C depending of the nature of the absorbent biomass of OMWW. Table 5 shows the different parameters that characterize the char oxidation stage of the impregnated samples (IS and ISW).

For instance, the IS first oxidation step takes place between 300 °C to 460 °C and it is attributed to the sawdust char oxidation. Likewise, ISW first oxidation occurs between 332–500 °C and corresponds to olive mill solid waste char. The second one between 460 °C to 570 °C for IS and between 500 °C and 620 °C for ISW is assigned to the char oxidation of polyphenol content in OMWW.

As shown on Fig. 4(b) and on Table 5, impregnated samples are oxidized with the same mass loss rate (0.055% s^{-1}) during the first step of oxidation. However, for ISW the last step takes place at high temperature with a higher weight loss mass rate (0.1180% s^{-1}) compared to the IS one (0.0064% s^{-1}). This behaviour may be attributed to the particle size of the impregnated biomass since sawdust has smaller particles (0.5 mm $< d <$ 0.7 mm) as compared to OMSW (1 $< d <$ 1.6 mm). In fact, many authors [26,27] noted that the particle size has an influence on the oxidation behaviour of OMSW and packed wood bed. Chouchene et al. [26] found that the char oxidation of the smallest sample ($d <$ 0.5 mm) occurs at lower temperature than for larger OMSW particle sizes (1 $< d <$ 1.6 mm) and (2 $< d <$ 2.8 mm). Moreover, Thunman et al. [27] showed that the rate of propagation of the reaction front through the fuel bed is lower for larger particles than for smaller ones. They attributed this behaviour to a temperature difference between the gas and the surface of the solid fuel in a bed packed with larger particles.

Table 6
Kinetic parameters of IS, ISW, sawdust, OMSW and OMWW-DM under inert atmosphere.

Sample	Active zone			Passive zone		
	Ea (kJ mol^{-1})	Ln (A (s^{-1}))	n	Ea (kJ mol^{-1})	Ln (A (s^{-1}))	n
IS	41.7	2.8	0.5	34.2	−14.0	0.08
ISW	37.3	1.3	0.6	9.7	−5.4	0.4
OMWW-DM	73.8	11.4	1.0	41.0	−15.5	0.06
Sawdust	80.6	10.4	0.7	27.2	−11.8	0.11
OMSW	35.3	0.9	0.6	55.9	−17.35	0.07

Oxidations of OMSW, sawdust, IS and ISW are completed at 400 °C, 450 °C, 550 °C and 620 °C, respectively. The residual mass obtained at 850 °C for OMWW-DM (13% ± 1) is higher than ISW (8.5% ± 0.6), IS (6% ± 1), OMSW (2.4% ± 0.5) and sawdust (2.1% ± 0.6). Residual masses at 850 °C correspond to ash contents. These values are close to those obtained in Table 2.

3.3. Kinetic parameters

Kinetic parameters of the reaction were determined using the procedure applied by Karaosmanoglu et al. [28]. During the analysis, w_0 is the original biomass sample decomposed to instantaneous sample mass w at time t. Hence, the rate can be written as a function of the weight conversion ratio, χ, over time t. The conversion ratio is defined as:

$$\chi = \frac{w_0 - w}{w_0 - w_f} \tag{1}$$

where w_f is the residue mass at the end of the process. The fundamental rate equation used in all kinetic studies is generally given as:

$$\frac{d\chi}{dt} = kf(\chi) \tag{2}$$

where, k is the rate constant and $f(\chi) = (1-\chi)^n$; where n is the order of reaction. According to the Arrhenius correlation, the rate constant k is defined as:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, E the activation energy, R the gas constant and T the reaction temperature. Thus, we can write Eq. (1) as:

$$\frac{-1}{w_0 - w_f}\frac{dw}{dt} = k\left(\frac{w - w_f}{w_0 - w_f}\right)^n \tag{4}$$

The combined eqs. (3) and (4) lead to a linear form equation:

$$Ln\left[\frac{-1}{w_0 - w_f}\frac{dw}{dt}\right] = Ln(A) - \left(\frac{E}{RT}\right) + nLn\left(\frac{w - w_f}{w_0 - w_f}\right) \tag{5}$$

Eq. (5) may be written in the linear form as:

$$y = B + Cx + Dz \tag{6}$$

where $y = Ln[-1/w_0 - w_f\,dw/dt]$, $x = 1/T$, $z = Ln(w - w_f/w_0 - w_f)$, $B = Ln(A)$, $C = -E/R$, $D = n$

Table 7
Kinetic parameters of IS, ISW, sawdust, OMSW and OMWW-DM under oxidative atmosphere.

Sample	Devolatilization step			Oxidation step					
				1st oxidation step			2nd oxidation step		
	Ea (kJ mol^{-1})	Ln (A (s^{-1}))	n	Ea$_1$ (kJ mol^{-1})	Ln (A_1 (s^{-1}))	n_1	Ea$_2$ (kJ mol^{-1})	Ln (A_2 (s^{-1}))	n_2
IS	48.4	4.7	0.6	91.2	10.3	1	—[a]	—[a]	—[a]
ISW	40.6	2.4	0.8	79.7	6.9	0.7	—[a]	—[a]	—[a]
OMWW-DM	62.8	8.3	0.8	—[a]	—[a]	—[a]	118	9.5	0.7
Sawdust	107.8	17.4	1	87.5	9.5	0.9	—[a]	—[a]	—[a]
OMSW	39.7	2.3	0.6	124.9	16.5	0.9	—[a]	—[a]	—[a]

[a] Values could not be calculated.

Constants *B, C, D* were estimated by multi-linear regression of the TGA data for each stage using Microsoft Excel.

The results of the kinetic parameters (pre-exponential factor, activation energy and reaction order) for each sample during pyrolysis are reported in Table 6. The main pyrolysis is named in literature as an active zone while the slow degradation is named as the passive zone [29]. As shown in Table 6, IS, ISW and OMSW have similar calculated values of activation energy. Thus, the degradation of OMSW was not influenced by the presence of OMWW under inert atmosphere. This is in agreement with results obtained from DTG plots. Moreover, a similar reaction order was observed for those samples. These values are comparable to values found by Chouchene et al. for OMSW [26]. However, sawdust and OMWW-DM activation energies are higher compared to the other samples.

The results of the kinetic parameters of each sample during devolatilization and oxidation steps under oxidative atmosphere are shown in Table 7.

It is clear that activation energy values obtained for IS and ISW during the devolatilization step are closer to the ones found during pyrolysis. Hence, the addition of OMWW and the presence of oxygen do not significantly influence the kinetic parameters during the devolatilization stage for impregnated samples, OMSW and OMWW-DM. In contrast, activation energies and pre-exponential factors were increased in the oxidation stage compared to the devolatilization. Table 7 reveals that ISW has the lowest values of activation energy during the two stages of degradation. During the second step of oxidation, kinetic parameters cannot be calculated for the impregnated samples by this kinetic model. However, OMWW-DM oxidation obtained the highest activation energy at a higher temperature. This result confirmed that the thermal degradation of OMWW-DM occurred at a higher temperature.

3.4. *Gaseous emissions analysis*

In order to obtain further information on the oxidation process, combustion tests were performed in a fixed bed reactor to analyse

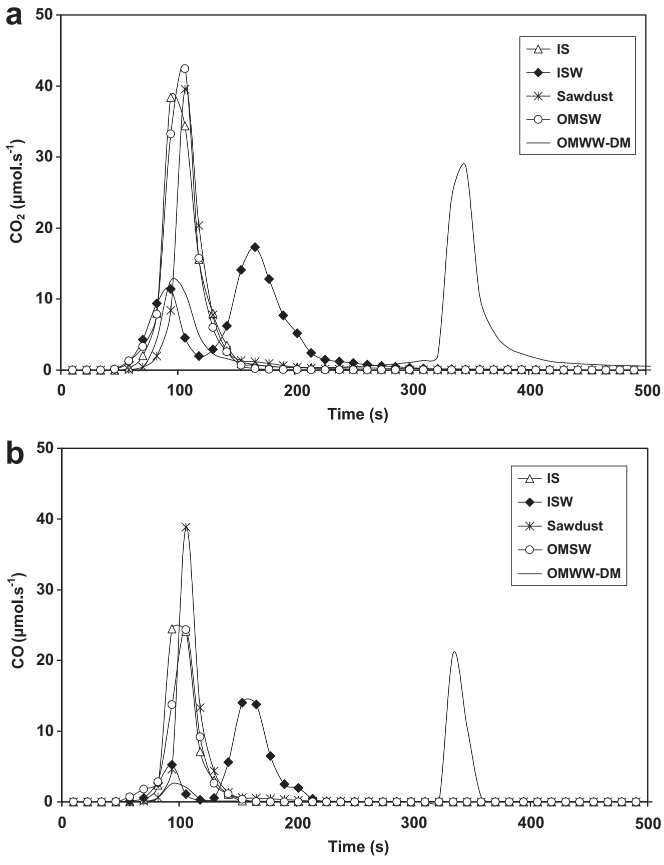

Fig. 5. Carbon dioxide (a) and carbon monoxide (b) emissions during the combustion of IS 40, ISW 40, sawdust, OMSW and OMWW-DM at 600 °C.

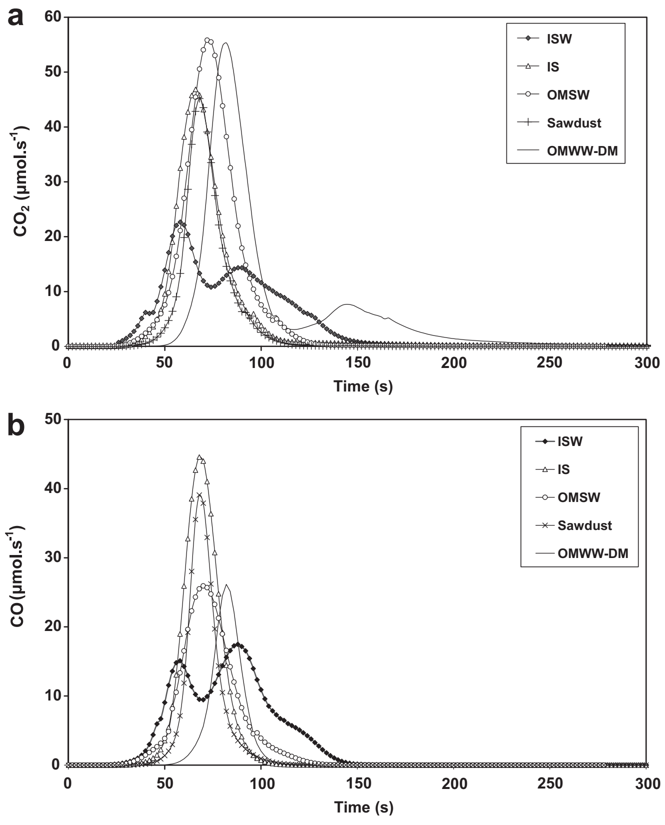

Fig. 6. Carbon dioxide (Fig .5a) and carbon monoxide (Fig .5b) emissions during the combustion of IS 40, ISW 40, sawdust, OMSW and OMWW-DM at 700 °C.

Table 8
Reaction time, carbon balance and gaseous emissions of IS, ISW, sawdust, OMSW and OMWW-DM at different temperature.

Sample	T °C	Δt, reaction time (s)	VOC (mmol g^{-1})	CO_2 (mmol g^{-1})	CO (mmol g^{-1})	Carbon balance (%)
IS	500 °C	226	2.9 (±0.1)	13 (±1)	8 (±1)	63.5
	600 °C	163	3.0 (±0.1)	13 (±1)	8 (±1)	66.3
	700 °C	161	3.2 (±0.1)	13 (±1)	10 (±1)	72
ISW	500 °C	422	2.6(±0.2)	12.8(±0.8)	5.6(±0.1)	55.8
	600 °C	294	2.6(±0.1)	13.1(±0.2)	8(±1)	62
	700 °C	218	3.5(±0.2)	12.4(±0.4)	9(±1)	65.2
OMSW	500 °C	260	2.8 (±0.3)	13.2(±1)	6 (±1)	50.3
	600 °C	253	4.2(±0.6)	15 (±1)	7.2 (±0.4)	59.7
	700 °C	160	4.9(±0.2)	16 (±2)	8.7 (±0.5)	67.6
Sawdust	500 °C	353	2.5 (±0.2)	13.7 (±0.2)	8.6 (±0.2)	64
	600 °C	180	2.9 (±0.3)	14.2 (±0.4)	10.5 (±0.2)	71
	700 °C	170	3.2 (±0.2)	16.3 (±0.2)	11.2 (±0.2)	79
OMWW-DM	500 °C	677	2.3 (±0.1)	5.1 (±0.4)	0.7 (±0.1)	23
	600 °C	504	2.5 (±0.2)	17.3(±0.7)	4 (±1)	68
	700 °C	262	3.5 (±0.2)	18.2(±0.5)	4.6 (±0.5)	75

the release of carbon oxides and volatile organic compounds at 500 °C, 600 °C and 700 °C.

Carbon dioxides emissions for IS and ISW as well as for the raw samples during the combustion at 600 °C are examined in Fig. 5.

As shown on Fig. 5, ISW and OMWW present different behaviours during their thermal treatment compared to IS, sawdust and OMSW at 600 °C. In fact, emission of carbon oxides shows two emission peaks of CO and CO_2 for ISW and OMWW-DM. Second CO and CO_2 releases for these samples are observed 1 min and 6 min after their first release peaks, respectively. Hence, the absorption of OMWW-DM on OMSW shifts their thermal process to a higher temperature. Although IS and ISW have the same amount of organic component from OMWW (40 wt%), ISW combustion occurs differently from IS combustion. This can be attributed to initial composition of biomass or to absorbent particle size.

To improve the combustion of ISW 40, thermal degradation of impregnated samples (ISW 40 and IS) is carried out at 700 °C. The Fig. 6 compares CO_2 and CO emission rates of IS and ISW 40 at 700 °C.

Carbon oxides emission rates of ISW show an overlapping of the two steps, while IS maintained the same profile at 700 °C. In fact, the increase of combustion temperature reduces the time between the two peaks during ISW combustion.

In order to have more information about the combustion of the different samples, gaseous emissions, reaction time and carbon balance of impregnated samples (IS and ISW), sawdust, OMSW and OMWW at different temperature are given in Table 8.

With regard to Table 8, the significant difference is the reaction time of the thermal degradation. The obtained values are lower for IS compared to ISW for all the tested temperature.

Emission quantities of CO_2, CO and VOC are not affected by the increase of temperature during the combustion of different samples, except for OMWW-DM. The combustion of this sample releases lower gaseous emissions at 500 °C. This shows that OMWW-DM is not oxidized at 500 °C.

All samples have produced similar amounts of CO, CO_2 and VOC, in particular at 600 °C. Therefore, the presence of OMWW simply causes the oxidation process to occur at higher temperature for ISW. This behaviour is due to the presence of aromatic compounds. Oxidation of these produces a char which requires higher temperatures to obtain complete oxidation [11].

As observed in Table 8, the carbon balance increases with temperature. In fact, carbon balance is between 63.5% and 72% for IS and it varies from 55.8% to 65.2% for ISW.

It is important to note that the increase of temperature increases CO and VOC emissions. This result may be attributed to the lower residence time and to a bad mixing between the air and the volatiles [30].

4. Conclusions

Olive mill wastewater (OMWW) was considered as a major pollutant, causing severe environmental threats. A combined process which includes absorption on low-cost renewable absorbents, Sawdust and Olive Solid Waste (OMSW), followed by energy recovery via combustion was studied. Thermal behaviour of absorbent impregnated with OMWW was studied under inert and oxidative atmosphere from 20 °C to 900 °C by thermogravimetric analysis (TGA). Kinetic parameters were determined for the pyrolysis reaction step for all samples. However, under an oxidative atmosphere and during the second step of oxidation, the activation energies of impregnated samples could not be obtained by the kinetic model used. Another model would be needed to understand the reaction mechanism at higher temperatures.

Gaseous emissions such as CO_2, CO and volatile organic compounds (VOC) were measured under oxidative conditions at 500 °C, 600 °C and 700 °C in a fixed bed reactor. The presence of OMWW in sawdust and olive solid waste mixtures increases the reaction time of the oxidation process compared to original sawdust and OMSW. High temperatures are necessary to achieve the thermal oxidation. Nevertheless, endpoint temperatures for both IS and ISW are close to those found in domestic boilers. The obtained results indicate that the reaction time of the thermal degradation of ISW is longer than for IS containing the same percentage of OMWW. Hence, the reduction of the amount of OMWW absorbed in ISW or the increase of the combustion temperature may provide a way to use the OMSW as an absorbent for OMWW.

The impregnation of OMWW on sawdust may be promising method of reduction of the environmental impact and energetic valorization of the organic content of OMWW. However, further investigations are necessary to optimize the sawdust/OMWW ratio.

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